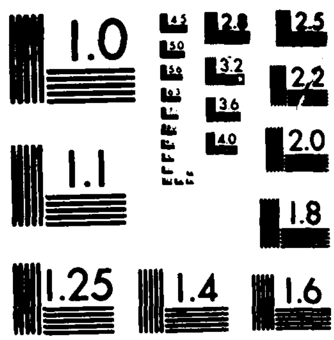
AD-A183 689 MODIFICATION OF THE STRUCTURE OF AMORPHOUS DIRECTIONAL 1/1
POLYMETHYL METHACR..(U) FOREIGN TECHNOLOGY DIV
WRIGHT-PATTERSON AFB OH A I KURILENKO ET AL. 14 AUG 87
UNCLASSIFIED FTD-ID(RS)T-0647-87 F/G 7/6 NL

END
9-87
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963-A

FTD-ID(RS)T-0647-87

FOREIGN TECHNOLOGY DIVISION

MODIFICATION OF THE STRUCTURE OF AMORPHOUS DIRECTIONAL POLYMETHYL METHACRYLATE BY METHODS OF GRAFTED AND BLOCK POLYMERIZATION

by

A.I. Kurilenko, V.P. Yakimtsov, L.P. Krul'

87 8 25 114

PARTIALLY EDITED MACHINE TRANSLATION

FTD-ID(RS)T-0647-87 14 August 1987

MICROFICHE NR: FTD-87-C-000636

MODIFICATION OF THE STRUCTURE OF AMORPHOUS DIRECTIONAL POLYMETHYL METHACRYLATE BY METHODS OF GRAFTED AND BLOCK POLYMERIZATION

By: A.I. Kurilenko, V.P. Yakimtsov, L.P. Krul'

English pages: 10

Source: Doklady Akademii Nauk SSSR, Vol. 204, Nr. 2, 1972, pp. 412-415

Country of origin: USSR
This document is a machine translation.
Input by: Eva R. Johnson
Merged by: Vicky L. Tipton
Requester: FTD/TQTR
Approved for public release; Distribution unlimited.

THIS TRANSLATION IS A RENDITION OF THE ORIGINAL FOREIGN TEXT WITHOUT ANY ANALYTICAL OR EDITORIAL COMMENT. STATEMENTS OR THEORIES ADVOCATED OR IMPLIED ARE THOSE OF THE SOURCE AND DO NOT NECESSARILY REFLECT THE POSITION OR OPINION OF THE FOREIGN TECHNOLOGY DIVISION.	PREPARED BY: TRANSLATION DIVISION FOREIGN TECHNOLOGY DIVISION WPAFB, OHIO.

MT TRANSLATION CORRECTIONS

As you use this document you may see technical translations which are incorrect or less than optimum. Translation Division personnel will be grateful for any corrections you forward to us. The next page contains blanks for your convenience in recommending better technical translations.

We need three things: the incorrect or poor translation, the correct or improved word or phrase, and the foreign page number.

Example:

Translation # FTD-ID(RS)T-0204-86 (Provided by SIT)

Foreign Page # ______________

Incorrect word/phrase: ____

____

Recommendation: ____

____

Foreign page numbers occur in the English text and may be found anywhere along the left margin of the page as in this example:

> In them occurs the state named "night blindness" - hemeralopia, which, according to the current point of view, is a result of damage of the rod-shaped apparatus of the eye.
>
> Page 51.
>
> However, in recent years it has been shown that with the hereditary pigment degenerations in animals the biochemical changes are observed in all celluar elements of the retina.

Remove the sheet with your recommendations from the translation and forward it to:

SITR/Mr Koolbeck/76538

The dictionary modification process requires from six weeks to six months to accomplish; therefore it will be some time before the results of your recommendations will be evident in translations.

We thank you for your assistance in improving the machine translation product.

TRANSLATION # FTD-ID(RS)T-0647-87

Foreign Page # ____________

Incorrect word/phrase: ____________________

____

Recommendation: ____________________

____

Foreign Page # ____________

Incorrect word/phrase: ____________________

____

Recommendation: ____________________

____

Foreign Page # ____________

Incorrect word/phrase: ____________________

____

Recommendation: ____________________

____

Foreign Page # ____________

Incorrect word/phrase: ____________________

____

Recommendation: ____________________

____

U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	$\sinh^{-1}$
cos	cos	ch	cosh	arc ch	$\cosh^{-1}$
tg	tan	th	tanh	arc th	$\tanh^{-1}$
ctg	cot	cth	coth	arc cth	$\coth^{-1}$
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

GRAPHICS DISCLAIMER

All figures, graphics, tables, equations, etc. merged into this translation were extracted from the best quality copy available.

MODIFICATION OF THE STRUCTURE OF AMORPHOUS DIRECTIONAL POLYMETHYL METHACRYLATE BY METHODS OF GRAFTED AND BLOCK POLYMERIZATION.

A. I. Kurilenko, V. P. Yakimtsov, L. P. Krul'.

(Presented by academician P. A. Rehbinder 30 September 1971).

Are in detail studied chemical aspects of problem of modification of properties of oriented crystalline polymeric materials by methods of synthesis in them of grafted and block copolymers and it is established that graft polymers are formed in amorphous zones of materials; however, mechanism of their effect on structure and mechanical properties of material is not clear [1, 2]. To model these processes is convenient in the amorphous polymeric materials, in which the oriented structures are not fixed/recorded by crystals, and therefore are more sensitive to any effects; the results of studying the processes of the grafted copolymerization in them and its effect on the structure and the properties of materials to more easily analyze. However, in the literature there is no information even about attempts at the realization of the grafted copolymerization in the oriented amorphous materials, probably, because the first stage of process - the sorption of monomer by material - leads to the relaxation of the oriented structures. By the analysis of the indirect data about the properties of the grafted materials is substantiated the mechanism of "cross-linking" of materials by the structures of grafted chains [3]. Consequently, it is possible to select conditions, with which the relationship/ratio of the rates of the synthesis of graft polymer (PP) and sorption of monomers provides the effective cross-linking of the oriented amorphous materials earlier than in them the concentration of monomer, sufficient for the plastification, will be accumulated. The realization of this assumption could be the direct proof of the correctness of the assumed mechanism of cross-linking and its universality and, furthermore, would reveal the possibility of amorphous materials by the methods of the grafted copolymerization.

In this work processes of grafted and block polymerization of polyacrylonitrile (PAN) and polyvinylidene chloride (PVDKh) in amorphous films of atactic polymethyl methacrylate (PMMA), oriented by extract, are studied. The selected polymers possess the combination of the properties, necessary for checking the assumptions presented. Oriented PMMA has heterogenic fibrillar structure [4] (as crystalline materials) and is readily soluble in AN and VDKh. PVDKh in the process grafting is crystallized and it reproduces well the oriented structures of the materials of any nature [6], PAN - is cross-linked during the heating, both more heat- and temperature-resistant, than PMMA, and they are not dissolved in the monomers.

To graft they conducted from gaseous phase by method of straight/direct generation of free radicals (γ-rays Co^{60}, rate of dose of 150 rad/s, T=25°) in samples, placed into medium of AN and VDKh, and by method of post-polymerization (samples No's 6, 7). Pressure of

AN and VDKh was selected so that the rates of synthesis would be close ones. The structure of samples studied by methods of IKS [expansion uncertain; may be infrared spectrophotometry] in polarized light (R - the value of dichroic relation for ν 536 cm^{-1} - PVDKh, 2248 cm^{-1} - PAN, 752 cm^{-1} - PMMA), isometric heating [5] and DTA [differential thermal analysis].

Page 413.

The quantity of PAN and PVDKh (ΔP) they are expressed in the percentages of weight of PMMA. The results of investigations are given in Table 1 and Fig. 1 and 2.

Grafted PMMA retains oriented structures and possesses properties of three dimensional polymers independent of nature and conditions of synthesis of graft polymer, which is evident from results of studying of solubility (at 20°) and thermomechanical properties.

In dichloroethane (solvent PMMA) samples No 2 and No 4 became stratified (isolated layers they are designated as samples No's 3 and 5), No 6 only will swell, and from No 7 is extracted ~30% PMMA. In the dimethyl formamide (solvent PMMA and PAN) samples No's 2, 5, and 7 are dissolved completely, but after heating during 15 min. at 160° they behave just as in the dichloroethane. With heating the fixed/recorded along the length samples in them are developed and increase with an increase in the temperature the internal stresses/voltages, caused by the entropy elasticity of the defrosted oriented structures of PMMA [7]. Maximum stresses/voltages σ_{max} in initial PMMA are observed when $T_{max}=80°$, further temperature rise causes decrease σ as a result of relaxing the structures and at 133° sample disintegrates. In grafted samples with σ_{max} higher than in the original and when $T>T_{max}$ is maintained at the same level to $T_{p}'=150°$ (samples No's 5, 6). Sharp decrease σ_{n} occurs only when $T_{p}=190-245°$, the samples with PAN retain their form and small σ, that grow at 350-400°.

From results of these experiments it unambiguously follows that grafted PMMA possesses structure of oriented three dimensional polymers, in which as the cross-links serve structures (blocks) of PAN and PVDKh, chemically combined with macromolecules of PMMA and fixing them until blocks are softened by heating or solvents. PAN during the heating chemically is cross-linked; therefore blocks of PAN do not disintegrate.

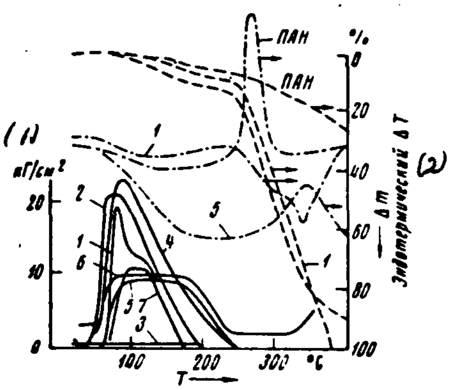


Fig. 1.

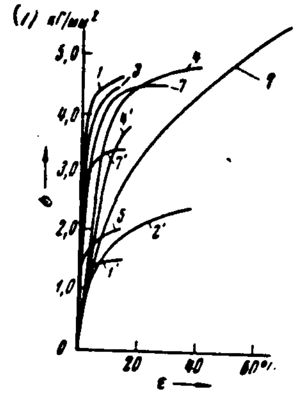


Fig. 2.

Fig. 1. Heat- and heat resistance of grafted films. Numerals in the curves correspond to the numbers of samples in Table 1. Diagrams of isometric heating - solid lines, thermogravimetric curves - dash (Δm - the decrease in weight of sample); thermogram - dot-and-dash lines.
Key: (1). kgf/cm². (2). Endothermal ΔT.

Fig. 2. Stress-strain diagrams of samples at 20°. 1, 2, 4, 7 - to the heating, 1', 2', 4', 7 ' - after heating at 160°, 15 min. Numerals in the curves correspond to the numbers of samples in Table 1.
Key: (1). kg/mm².

Page 414.

Since PMMA is destroyed in a field of γ-radiation [8] and its oriented structures relax during sorption of small quantities of vapors of monomers, this also testifies about high effectiveness of processes of transforming growing grafted chains into blocks, which fix macromolecules of PMMA, and confirms volumetric character of processes of synthesis of PAN and PVDKh even under conditions of severe diffusion conditions of realization by its direct method. Basis ΔP is formed not in the adsorptive layer on the external surface of film, but within. In the sample the concentration gradient of monomer, which decreases from the surface into the depth, is created. In the beginning of process the inner layers, not yet softened by monomer, serve as the base, which retains the sizes/dimensions of sample; subsequently the grafted structures of PAN and PVDKh reinforce material and they prevent the relaxation of the oriented structures of PMMA during the heating and in the solvents. Under the given conditions the layers with a thickness of 20-30μ effectively are cross-linked; therefore in samples No's 2 and 4 (d=170 μ) middle layers are soluble, and the outer grafted layers (samples No's 3, 5) are separated/liberated.

Laminated structure of samples No's 2, 4 reflects their DIN [expansion unknown] (Fig. 1), form of which is obtained as if imposition of DIN prototype and grafted throughout entire volume sample. The isolated by solvent layers of PMMA with CCPAN (sample No 5) retain orientation, but with PVDKh (sample No 3) - no. Lower effectiveness of PVDKh, possibly, is connected with the formation of larger/coarser structures of PVDKh, i.e., with the smaller concentration of blocks in the sample with ΔP, commensurate with PAN. Analogously, it is possible to explain the capacity of PVDKh to form the oriented structures (R=1.4) during synthesis PAN R=1.05 under the same conditions).

Strength (σ_p^t) of grafted samples No's 2, 4, 7 is not lower than initial, although they contain significant quantities of PAN and PVDKh (ΔP) and breakdown elongations (ε_p) of them somewhat above. After heating (15 min., 160°) the grafted samples to the greater degree retain σ_p^t and ε_{p}, than initial (especially in grafted evenly by the volume of the sample, which retains a certain strength even at 160°). This also confirms conclusion about formation in PMMA of the effective cross-linkings, which raise the heat capacity of material.

Table 1. Structure and the property of the grafted oriented films of polymethyl methacrylate.

№	(1) Образец				(2) Термомеханические свойства							(5) Механические свойства			
	d, μ	ПП	ΔP, %	R	$T_н$, °C	T_{max}, °C	T'_p, °C	T_p, °C	σ_{max}, кГ/мм² (3)	(3) $\sigma_{max}^{ПММА*}$, кГ/мм²	E_∞^{**}, кГ/см² (4)	ε_p, %	σ_p^ε, кГ/мм² (3)	$(\sigma_p)_T^{***}/\sigma_p$	$(\varepsilon_p)_T^{***}/\varepsilon_p$
1	70	—	—	1,3	63	83	—	133	0,200	0,200	0	20	5,5	0,27	0,40
2	170	ПВДХ	28	1,4	59	80	—	218	0,252	0,297	—	70	8,8	0,40	0,57
3	20	ПВДХ	—	1,4	—	—	—	—	0	—	—	11	2,0	—	—
4	170	ПАН	18	1,04	64	90	—	245	0,235	0,278	—	35	5,6	1,4	1,4
5	30	ПАН	—	—	65	83	150	220	0,092	—	—	12,5	4,5	—	—
6	70	ПАН	75	1,06	63	83	155	—	0,135	0,238	0,45	—	—	—	—
7	80	ПАН	9	—	75	100	—	190	0,095	0,098	0,05	30 (40)	5,6 (0,035)	0,66	0,5

Key: (1). Sample. (2). Thermomechanical properties. (3). kg/mm². (4). kgf/cm². (5). Mechanical properties.

FOOTNOTE [1]. $\sigma_{max}^{ПММА}$ - relation σ_{max} and to fraction/portion of PMMA in the grafted sample.

[2]. Equilibrium modulus at 180°.

[3]. $(\sigma_p)_T, (\varepsilon_p)_T$ - tensile strength and elongation after aging of samples at 160° of 15 min. In the parentheses the results of strength tests at 160°. ENDFOOTNOTE.

Page 415.

During heating to 300-400° are cross-linked with PAN samples they change chemical nature, which evidently from results of study (Fig. 1) by method of DTA of PMMA is destroyed and sample, without changing form, is converted into polyene cross-linked thermoresistant material, i.e., in principle prototype of PMMA is matrix/die for direct synthesis in it of polymeric material of another structure.

Thus, study of properties and structure of grafted oriented amorphous PMMA made it possible to demonstrate validity of proposed into [3] mechanism of cross-linking polymers by blocks of grafted chains. Furthermore, is established/installed the possibility of the effective cross-linking of the oriented amorphous materials by the graft polymers, whose structures can fulfill the functions of crystallites, which offers essentially new possibilities of the modification of the physicochemical and mechanical properties of the oriented polymeric amorphous materials with the synthesis in them of the "crystallites" of the graft polymers of necessary nature with the optimal according to the sizes and by the volume of materials.

REFERENCES.

1. G. Batterd, D. U. Treger. Properties of grafted and block copolymers, 1970.

2. G. A. Kleyn, L. Kh. Osipova et al. Effect of nuclear radiations and radiation inoculation on fibers, M., 1968.

3. A. I. Kurilenko, DAN, 203, No 5 (1972).

4. S. N. Zhurkov, V. A. Marikhin et al. High-molec. compounds, 4, 282 (1962).

5. A. I. Kurilenko, V. A. Temnikovskiy, S. L. Dobretsov, Mech. polym., No 6, 963 (1967).

6. N. Kh. Fayzi, A. N. Kurilenko, High-molec. compounds, B13, 216 (1971).

7. L. A. Layus, Ye. V. Kuvshinskiy, Mech. polym., No 2, 163 (1966).

8. A. Charl'zbi, Nuclear radiations and polymers, IL, 1962.

Belorussian state university im. V. I. Lenin, Minsk.

Received 1 July 1971.

DISTRIBUTION LIST

DISTRIBUTION DIRECT TO RECIPIENT

ORGANIZATION	MICROFICHE
A205 DMAHTC	1
A210 DMAAC	1
B344 DIA/RTS-2C	9
C043 USAMIIA	1
C500 TRADOC	1
C509 BALLISTIC RES LAB	1
C510 R&T LABS/AVRADCOM	1
C513 ARRADCOM	1
C535 AVRADCOM/TSARCOM	1
C539 TRASANA	1
C591 FSTC	4
C619 MIA REDSTONE	1
D008 NISC	1
E053 HQ USAF/INET	1
E404 AEDC/DOF	1
E408 AFWL	1
E410 AD/IND	1
E429 SD/IND	1
P005 DOE/ISA/DDI	1
P050 CIA/OCR/ADD/SD	2
AFIT/LDE	1
FTD	
CCN	1
NIA/PHS	1
LLNL/Code L-389	1
NASA/NST-44	1
NSA/1213/TDL	2
ASD/FTD/TQIA	1

END
9-87
DTIC